Syntheses and crystal structures of a covalent trialkylantimony hydroxo bromide and related trialkylantimony(V) halides

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Abstract

R_3SbBr_2 (**1**), RMe_2SbBr_2 (**2**), or RMe_2SbI_2 (**3**) [R = $(Me_3Si)_2CH$] are formed by addition of Br_2 or I_2 to R_3Sb or RMe_2Sb. $(Me_3SiCH_2)_3Sb(Br)OH$ (**4**) is obtained by hydrolyzing **1** or $(Me_3SiCH_2)_3SbBr_2$. The crystal structures of **1**, **3**, **4** and $[(Me_3SbBr)_2]O$ (**5**) [Me = CH_3] have been determined. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Antimony; Bromine; Iodine; X-ray structure

1. Introduction

Triorganoantimony(V) dihalides, R_3SbX_2 [R = alkyl, aryl; X = Cl, Br, I] are important reagents in the organometallic chemistry of antimony, which have been used for the synthesis of diorganoantimony(III) halides by thermal elimination of RX or for hydrolytic reactions with formation of dihydroxides, or oxides, R_3SbO [1]. Intermediates of the hydrolyses are binuclear condensation products, $(R_3SbX)_2O$ [2] or hydroxy halides of the type $R_3Sb(OH)X$ [3,4], which exist with bulky organic groups. Only one example, the ionic species $[(2,6-Me_2C_6H_3)_3SbOH]^+ I^-$ with tetrahedral geometry was characterized by single crystal X-ray diffraction [4]. Also for triorganoantimony dihalides ionic structures, $[R_3SbX]^+ X^-$ are possible and an early report in 1938 described the crystal structures of Me_3SbX_2 [X = Cl, Br, I] as partially ionic [5]. A recent reinvestigation revealed, however, the highly symmetrical D_3h, non-ionic structure for Me_3SbBr_2 [6].

We report here on syntheses, reactions and structures of three trialkylantimony dihalides with the bulky bis(trimethylsilyl)methyl substituent: R_3SbBr_2 (**1**), RMe_2SbBr_2 (**2**), and RMe_2SbI_2 (**3**) [R = $(Me_3Si)_2CH$], on a covalent trialkylantimony hydroxo halide, $(Me_3SiCH_2)_3Sb(Br)OH$ (**4**), and on the structure of $(Me_3SbBr)_2O$ (**5**).

2. Results and discussion

The trialkylantimony dihalides **1**–**3** form as air stable solids in the usual way by reaction of Br_2 or I_2 with the corresponding tertiary stibanes. R_3Sb [R = $(Me_3Si)_2CH$] was obtained by complete alkylation of $SbCl_3$, which is more effective than the procedure we reported earlier [7]. RMe_2Sb [R = $(Me_3Si)_2CH$] is formed in the reaction between the Grignard reagent $MeMgI$ and $RSbCl_2$ in the 2:1 molar ratio. Attempts to use **2** as a source for the formation of $R(Me)SbBr$ by thermal elimination of $MeBr$ failed. Heating to 220 °C resulted mainly in distillation. The NMR spectra of **1** in $CDCl_3$ and of **2** and **3** in C_6D_6 at 20 °C show the expected signals for equivalent bis(trimethylsilyl)methyl or methyl substituents corresponding to the usual trigonal bipyramidal structures of covalent trialkylantimony dihalides with axial halogen atoms and equatorial alkyl groups. The ^1H and ^{13}C-NMR spectra of **1** in C_6D_6, in C_6D_6–$CDCl_3$ mixtures or in $C_6D_5CD_3$ are, however, surprisingly complex. Independent from variations of the temperature from + 70 to − 70 °C or the concentration there are four singlet signals of almost equal intensity for the methine protons and multiplets for the Me_3Si groups which become even more complex below

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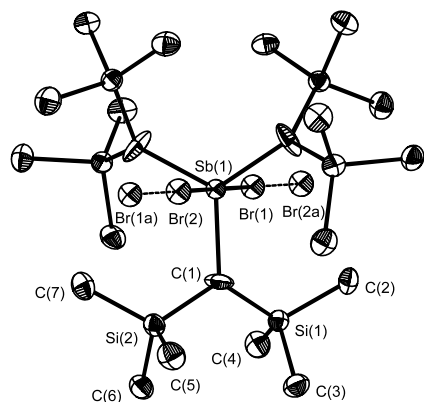*E-mail address:* breunig@chemie.uni-bremen.de (H.J. Breunig).

Fig. 1. ORTEP representation of **1** at 50% probability showing the atomic numbering scheme, together with two Br atoms of neighboring molecules. Selected distances (pm) and angles (°): Sb(1)–Br(1) 267.20(11), Sb(1)–Br(2) 264.57(11), Sb(1)–C(1) 214.9(5), Br(1)–Sb(1)–Br(2) 180.00(0), Br–Sb(1)–C(1) 88.4(2)–91.6(2), Sb–C–Si 119.5(3)–120.7(3), Br⋯Br 347.3(1).

− 20 °C. A similar pattern is also observed when the spectra of **1** in CDCl$_3$ are recorded at low temperatures between − 50 and − 70 °C.

These results clearly indicate that the solid state structure of **1** where all the (Me$_3$Si)$_2$CH substituents are equivalent (isomer **1a**) is not completely preserved in solution. The most straightforward interpretation of the solution NMR spectra is to assume the presence of an additional isomer **1b**, which is derived from the solid state form, **1a** by a 180° rotation of one of the

(Me$_3$Si)$_2$CH groups around the Sb–C bond. In **1b**, where two of the C–H groups are directed towards each other, the methine protons are not equivalent and three singlet signals should be expected. The distribution of intensities in the CH region of the experimental spectra suggests a 1:3 molar ratio for **1a** and **1b** in benzene or toluene in the range between − 70 and + 70 °C. The simplicity of the room temperature spectrum of **1** in CDCl$_3$ (two lines in the 1:18 ratio of intensities) is presumably due to an accidental isochrony of the signals of **1a** and **1b** and not to an exclusive preference for **1a** under these conditions.
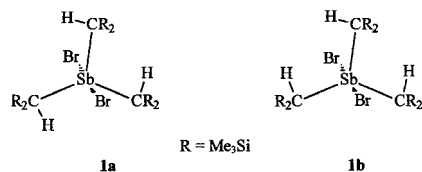
For solid **1** and **3** the trigonal bipyramidal structural type was confirmed by a single crystal X-ray diffraction study. The structures are depicted in Figs. 1 and 3. In the crystal the molecules of **1** are associated to columns through intermolecular Br⋯Br contacts of 347.3(1) pm. A packing diagram for **1** showing the arrangement of the columns is provided in Fig. 2. The inspection of the bond lengths and angles reveals that the D_3h geometry is represented with only small distortions in the central skeleton of **1**, with the Br–Sb–Br angle of 180°, the C–Sb–C angles of 119.92(2)° and Br–Sb–C angles be-
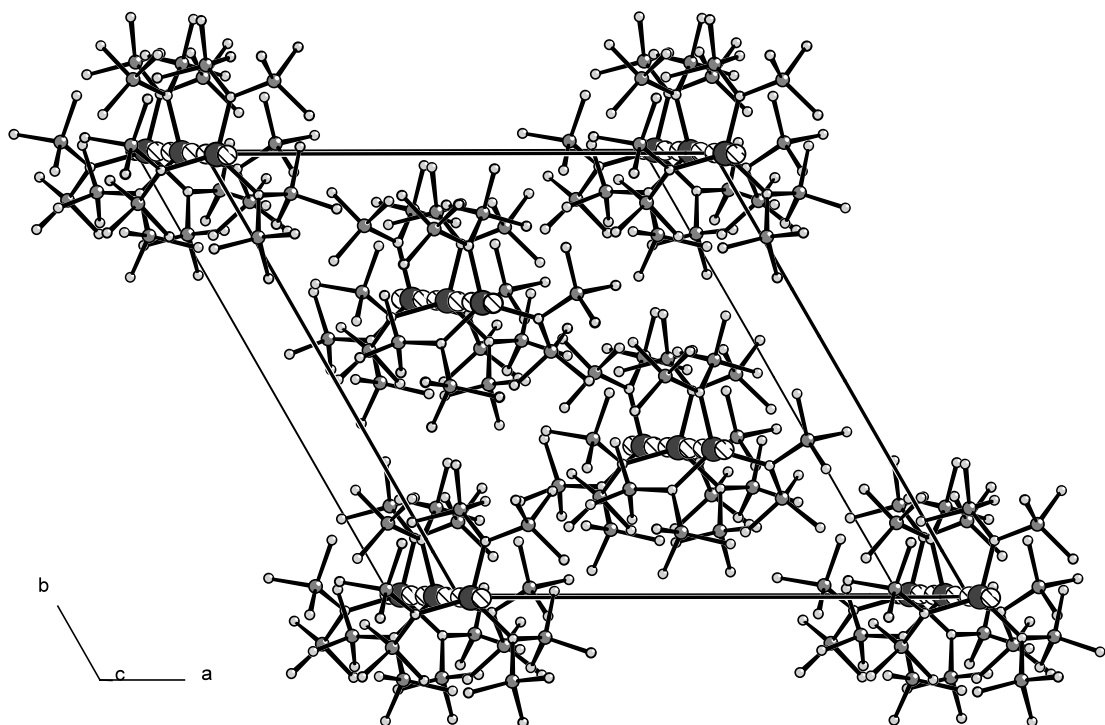

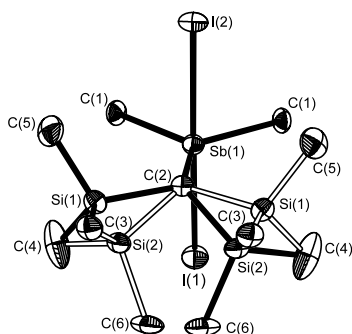Fig. 2. The crystal packing of **1** (down the *c* axis). Hydrogen atoms have been removed for clarity.

Fig. 3. ORTEP representation at 50% probability of **3** showing the atomic numbering scheme. Selected distances (pm) and angles (°): Sb(1)–C(1) 214.4(8), Sb(1)–C(2) 213.8(10), Sb(1)–I(1) 287.41(11), Sb(1)–I(2) 294.44(11), C(1)–Sb(1)–C(1′) 114.8(5), C(2)–Sb(1)–C(1) 122.4(2), C(2)–Sb(1)–I(1) 96.5(3), C(1)–Sb(1)–I(1) 90.1(2), C(2)–Sb(1)–I(2) 90.1(3), C(1)–Sb(1)–I(2) 86.4(2), I(1)–Sb(1)–I(2) 173.44(3).
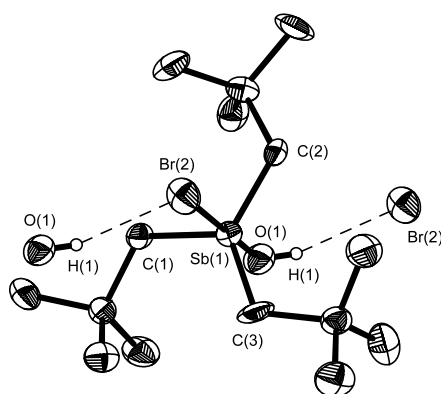

Fig. 4. ORTEP representation at 50% probability of **4** showing the atomic numbering scheme, together with the intermolecular O–H···Br interactions. Selected distances (pm) and angles (°): Sb(1)–O(1) 196.1(9); Sb(1)–C(1) 209.2(12); Sb(1)–C(2) 211.1(12); Sb(1)–C(3) 211.4(12); Sb(1)–Br(2) 287.26(17); O(1)–Sb(1)–C(1) 93.7(5); O(1)–Sb(1)–C(2) 95.2(4); O(1)–Sb(1)–C(3) 95.0(5); C(1)–Sb(1)–C(2) 120.1(5); C(1)–Sb(1)–C(3) 112.8(6); C(2)–Sb(1)–C(3) 125.1(6); O–Sb(1)–Br(2) 179.3(3); C(1)–Sb(1)–Br(2) 85.7(3); C(2)–Sb(1)–Br(2) 84.8(3); C(3)–Sb(1)–Br(2) 85.6(4), O(1)···Br(2) # 346.8(46).

tween 88.4(2) and 91.6(2)°. The comparison of the bond lengths of **1** [Sb–C: 214.9(5); Sb–Br: 264.6(1), 267.2 (1) pm] with Me_3SbBr_2 [Sb–C: 204.7(5); Sb–Br 264.9 pm] [6] shows that the Sb–C bonds are longer in **1**, whereas, the Sb–Br bond lengths have similar values in both compounds. The orientation of the alkyl group in **1** can be described as propeller like with H–C–Sb–Br torsion angles of 46.94(1)°.

Distortions from the ideal trigonal bipyramidal geometry are more pronounced in the structure of **3** with the parameters: Sb–I 287.4(1), 294.4(1); Sb–C 213.8(10)–214.4(8) pm, C–Sb–C 114.8(5)–122.4(2), C–Sb–I 86.4(2)–96.5(3), I–Sb–I 173.44(3)°. The Sb–I bond lengths compare well with the corresponding value in Ph_3SbI_2 [288.5 pm] [8]. A slight rotation (ca. 31°) around the Sb(1)–C(2) axis of **3** leads to a disorder

of the $CH(SiMe_3)_2$ group. The atoms Sb(1), C(2), I(1) and I(2) lie on a crystallographically effective mirror plane. Therefore there is only one independent $SiMe_3$-group. The disorder leads to two positions for the $SiMe_3$-groups, with 50% occupancy. The disordered $SiMe_3$-groups share the atoms C(3) and C(4), while one methyl group is assigned exclusively to a Si-atom [Si(1)–C(5), Si(2)–C(6)].

The hydrolysis of **1** was carried out with a solution of potassium hydroxide in water. Unexpectedly not only bromine atoms but also Me_3Si groups were substituted and the hydroxo bromide $(Me_3SiCH_2)_3SbBr(OH)$ (**4**) was obtained. Hydrolytic cleavage of Me_3Si-element bonds is common for many elements but a rare case for Si–C(alkyl) bonds which usually occurs only with very drastic conditions. The sterically congested situation and the electron withdrawing effect of the Sb(V) center may be responsible for the facile hydrolysis. A more rational synthesis of **4** [72% yield] is achieved by reacting $(Me_3SiCH_2)_3SbBr_2$ with potassium hydroxide in water. The novel hydroxo bromide is an air stable compound with little tendency to dehydrate to an oxo bridged binuclear species. The compound remains unchanged for 12 h at 60 °C under reduced pressure. Further heating leads to decomposition.

The presence of the hydroxo group in **4** is proven by the infrared spectra. In Nujol the v(O–H) band appears as a broad signal with a maximum of intensity at 3446 cm^{-1}. In CH_2Cl_2 solution the v(O–H) band is shifted to a higher frequency (3632 cm^{-1}) and becomes sharp. In contrast the frequency of the v(Sb–O) band is lower (542 cm^{-1}) in CH_2Cl_2 than in Nujol (581 cm^{-1}). These shifts indicate weak hydrogen bonding in the solid state. Similar values have been observed for $(C_6H_{11})_3Sb(OH)Br$ [in CH_2Cl_2, v(O–H) = 3628, v(Sb–O) 538 cm^{-1}] [3].

The ^{1}H- and ^{13}C-NMR spectra of **4** in C_6D_6 show the expected two singlet signals for the Me_3SiCH_2 groups but no signal for the OH protons. The crystal structure of **4** is depicted in Fig. 4. There is a slightly distorted trigonal bipyramidal coordination with angles Br–Sb–O 179.3(3)°, C–Sb–Br 84.8(3)–85.7(3)°, O–Sb–C 93.7(2)–95.2(4)°. The Sb–O(H) bond length [196.1(9) pm] lies in the usual range for covalent triorganoantimony(V) hydroxides, cf. $Mes_3Sb(OH)[O(O)CCHCl_2]$, Sb–O(H), 197.5(3) [9]; $Mes_3Sb(OH)_2$, 202.7(3) pm [10]. The Sb–Br bond in **4** [287.26(17) pm] is longer than in **1** [264.4(1)– 267.1(1)] or Me_3SbBr_2 [264.9 pm] [6]. The hydrogen atom of the hydroxyl group was not localized by X-ray diffraction. The closest intermolecular contacts exist between oxygen and bromine atoms of different molecules. The O···Br contact distances of 346.8(46) pm indicate weak intermolecular hydrogen bonds.

μ-Oxo-bis[trimethylbromoantimony(V)], **5** was obtained by hydrolysis of Me_3SbBr_2 with traces of moisture, or more efficiently by the well known reaction of
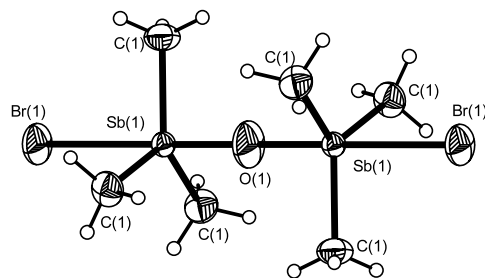
Fig. 5. ORTEP representation at 50% probability of **5** showing the atomic numbering scheme. Selected distances (pm) and angles (°): Sb(1)–O(1) 191.95(4); Sb(1)–C(1) 210.0(4); Sb(1)–Br(1) 284.41(9); O(1)–Sb(1)–C(1) 93.98(13); C(1)–Sb(1)–C(1) # 2 119.52(3); O(1)–Sb(1)–Br(1) 180.00(3); C(1)–Sb(1)–Br(1) 86.02(13); Sb(1) # 3–O(1)–Sb(1) 180.0.

$Me_3Sb(OH)_2$ with Me_3SbBr_2 [11,12]. The crystal structure was investigated on single crystals obtained from solutions in methanol. The molecular structure is shown in Fig. 5. There are two antimony centers with trigonal bipyramidal environments connected through a bridging oxygen atom. The methyl groups are in equatorial position in a staggered conformation and the bromine and oxygen atoms occupy the axial positions.

The Br–Sb–O and Sb–O–Sb angles are 180° and Sb–O bond lengths are 1.9195(4) Å. Similar values were reported for the analogous structure of $(ClMe_3Sb)_2O$ [Sb–O, 190.7(1) ppm] [13]. The Sb–Br bond in **5** [284.41(9) pm] is longer than in Me_3SbBr_2 [264.9 pm]. The bond angles O(1)–Sb(1)–C(1) 93.98(13), C–Sb–Br 86.02(13) are close to the ideal values. Crystallographic data of **1**, **3**–**5** are given in Table 1.

All the crystal structures reported here represent typical trigonal bipyramidal geometries. There are only slight distortions with elongations of one of the antimony halogen bonds and small inclinations of the

Table 1
Crystallographic data and measurements for **1**, **3**, **4**, **5**

Compound	1	3	4	5
Empirical formula	$C_{21}H_{57}Br_2SbSi_6$	$C_9H_{25}I_2SbSi_2$	$C_{12}H_{34}BrOSbSi_3$	$C_6H_{18}Br_2OSb_2$
Formula weight	756.75	565.02	480.32	509.51
Color	Colorless	Yellow	Colorless	Colorless
Crystal size (mm)	$0.5 \times 0.2 \times 0.2$	$0.5 \times 0.3 \times 0.3$	$0.4 \times 0.2 \times 0.1$	$0.5 \times 0.2 \times 0.2$
Unit cell dimensions				
a (pm)	1880.0(3)	1699.4(2)	670.4(1)	1122.9(1)
b (pm)	1880.0(3)	1699.4(2)	3145.3(6)	1122.9(1)
c (pm)	1757.5(4)	1248.0(3)	1056.6(2)	1122.9(1)
α (°)	90	90	90	90
β (°)	90	90	94.16(3)	90
γ (°)	120	90	90	90
Crystal system	Hexagonal	Tetragonal	Monoclinic	Cubic
Space group	$R3c$	$P4_2/mbc$	$P2(1)/n$	Pa-3
Z	6	8	4	8
Diffractometer	Stoe IPDS	Siemens P4	Stoe IPDS	Stoe IPDS
Mo–K_α (Å)	0.71073	0.71073	0.71073	0.71073
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Reflections collected	19 385	48 317	2241	456
Independent reflections	2373	1786	2241	456
R_{int}	0.0737	0.0613	0.0000	0.0000
Completeness to θ	99.1%	96.2%	68.1%	98.1%
Absorptions coefficient (mm^{-1})	3.207	4.584	3.194	9.423
Absorption correction	DIFABS	Empirical	Numerical	DIFABS
Final R^a indices [$I > 2\sigma(I)$]	$R_1 = 0.0328$ $wR_2 = 0.0905$	$R_1 = 0.0454$ $wR_2 = 0.1099$	$R_1 = 0.0567$ $wR_2 = 0.1330$	$R_1 = 0.0209$ $wR_2 = 0.0578$
R^a indices (all data)	$R_1 = 0.0398$ $wR_2 = 0.1086$	$R_1 = 0.0613$, $wR_2 = 0.1144$	$R_1 = 0.0794$ $wR_2 = 0.1401$	$R_1 = 0.0249$ $wR_2 = 0.0585$
Goodness of fit on F^2	1.157	1.103	0.919	1.075
$F(000)$	2310	2112	968	936
Data/restraints/parameters	2373/1/98	1786/0/95	2241/0/172	456/0/20
Index ranges	$-23 \leq h \leq 23$, $-23 \leq k \leq 23$, $-21 \leq l \leq 21$	$-20 \leq h \leq 20$, $-20 \leq k \leq 20$, $-14 \leq l \leq 14$	$-7 \leq h \leq 7$, $0 \leq k \leq 35$, $0 \leq l \leq 11$	$0 \leq h \leq 9$, $0 \leq k \leq 9$, $2 \leq l \leq 13$
Largest difference peak and hole (e $Å^{-3}$)	0.694 and -0.501	0.912 and -1.007	0.821 and -0.493	0.670 and -0.335
Refinement method	Full-matrix least squares on F^2 [14]			
Treatment of hydrogen atoms	Refined with a riding model and common isotropic temperature factor			

equatorial substituents towards the longer axial bond as expected for a partial ionic character.

3. Experimental

The syntheses of **1**–**4** were carried out in an argon atmosphere using dried solvents distilled under argon. The NMR spectra were recorded on a Bruker DPX 200 instrument. For the mass spectrometry a Finnigan MAT 8222 and for the IR spectra a FTIR SPEK-TRUM 1000 instruments were used.

3.1. Synthesis of tris[bis(trimethylsilyl)methyl]antimony and tris[bis(trimethylsilyl)methyl]antimony dibromide (**1**)

A solution of $(Me_3Si)_2CHCl$ (5.00 g, 25.7 mmol) in THF (10 ml) was added with stirring to lithium powder (0.54 g, 77.8 mmol, 50–200 μm) in boiling Et_2O (30 ml). The addition was completed after 1 h and the reaction mixture was stirred for 24 h with reflux. The solution was filtered and added at room temperature (r.t.) to freshly sublimed $SbCl_3$ (1.66 g, 7.26 mmol) in Et_2O (25 ml). After stirring for 16 h at r.t. the solvents were removed under reduced pressure and the solid residue was extracted with petroleum ether (2 × 120 ml). Removal of the petroleum ether gave 4.26 g (98%) of $[(Me_3Si)_2CH]_3Sb$, as a yellow solid which can be purified by sublimation at 110 °C/6×10^{-3} mbar. M.p. 80–82 °C. ^1H-NMR (C_6D_6, 200 MHz): 0.31 (s, 18 H, CH_3), 0.98 (s, 1H, CH). MS data as reported [7].

At -20 °C a solution of Br_2 (52 mg, 0.32 mmol) in Et_2O (20 ml) was added to $[(Me_3Si)_2CH]_3Sb$ (200 mg, 0.33 mmol) in 30 ml Et_2O. After the addition the mixture was allowed to warm up to r.t. Slow evaporation of the solvent gave 210 mg (84%) of **1** as colorless crystals melting at 174 °C. ^1H-NMR (CDCl$_3$, 200 MHz), 20 °C: 0.43 (s, 18 H, CH_3), 2.38 (s, 1 H, CH); -70 °C: 0.28 (m, 54 H, CH_3), 2.09, 2.23, 2.36, 2.57 (s, 1 H, CH). ^1H-NMR (C_6D_6, 200 MHz): 0.41 (m, 54 H, CH_3), 2.49, 2.60, 2.80, 2.91 (s, 1 H, CH). ^{13}C-NMR (C_6D_6, 50 MHz): 5.06 (s, CH_3), 5.14 (s, CH_3), 5.46 (s, CH_3), 5.63 (s, CH_3), 36.15 (s, CH), 37.37 (s, CH), 40.43 (s, CH), 42.51 (s, CH). MS (EI, 70 eV): 745 (5) [M$^+$–Me], 679 (41) [M$^+$–Br], 599 (3) [[(Me$_3$Si)$_2$CH]$_2$-SbBr$_2^+$], 505 (8) [[(Me$_3$Si)$_2$CH]$_2$SbBr$^+$–Me], 439 (32) [[(Me$_3$Si)$_2$CH]$_2$Sb$^+$], 361 (16) [[(Me$_3$Si)$_2$CH]SbBr$^+$], 273 (13), 207 (11) [(Me$_3$Si)CHSb$^+$], 129 (100) [(Me$_3$Si)$_2$-CH$^+$–2Me], 87 (49) [Me$_4$Si$^+$], 73 (100) [Me$_3$Si$^+$], 59 (36) [Me$_2$Si$^+$]. Anal. Found: C, 33.20; H, 7.55; Br, 21.00. $C_{21}H_{57}Si_3Br_2Sb$. Calc.: C, 33.20; H, 7.56; Br, 20.75%.

3.2. Syntheses of dimethyl[bis(trimethylsilyl)methyl]-antimony and dimethyl[bis(trimethylsilyl)methyl]-antimony(V) dibromide (**2**)

A solution of $(Me_3Si)_2CHSbCl_2$, (1.5 g, 4.26 mmol) in 30 ml Et_2O was added drop wise with stirring to a solution of MeMgI (1.54 g, 9.29 mmol), in 40 ml Et_2O. After the addition the mixture was stirred over night. The solvent was removed at reduced pressure and the white residue was extracted with petroleum ether (2 × 15 ml). Removal of the solvent in vacuum, gave 1.0 g (75.75%) of $Me_2[(Me_3Si)_2CH]Sb$ as a light yellow, air sensitive oil, b.p. 32 °C, 2×10^{-1} mbar. ^1H-NMR (C_6D_6, 200 MHz): 0.16 (s, 1H, CH), 0.13 (s, 18 H, CH_3), 0.79 (s, 6 H, CH_3); ^{13}C-NMR (C_6D_6, 50 MHz): -1.19 (CH$_3$), 2.31 (CH) 3.14 (CH$_3$–Si). MS (EI, 70 eV): 310 (25), [M], 295 (38), [M$^+$–Me], 207 (28) [(Me$_3$Si)CHSb$^+$], 129 (17) [(Me$_3$Si)$_2$CH$^+$–2Me], 73 (100) [Me$_3$Si$^+$]. Anal. Found: C 34.47; H 7.98. Calc.: $C_9H_{25}SbSi_2$: C, 34.73; H, 8.10%.

A solution of Br_2 (0.51 g, 3.18 mmol) in 10 ml Et_2O was added dropwise at 0 °C to a solution of $Me_2(Me_3Si)_2CHSb$ (1.0 g, 3.21 mmol) in 15 ml Et_2O. The mixture was stirred for 1 h. Slow evaporation of Et_2O gave 0.92 g (61.24%) of **2** as light yellow crystals, m.p.: 149–151 °C. ^1H-NMR (C_6D_6, 200 MHz): 0.21 (s, 18 H, CH_3), 1.89 (s, 1H, CH), 2.24 (s, 6 H, CH_3); ^{13}C-NMR (C_6D_6, 50 MHz): 2.59 (CH$_3$–Si), 30.59 (CH$_3$), 34.71 (CH); MS (EI, 70 eV): 455 (8), [M$^+$–Me], 391 (100), [M$^+$–Br], 129 (24) [(Me$_3$Si)$_2$CH$^+$–2Me], 73 (98) [Me$_3$Si$^+$]. Anal. Found: C, 22.74; H, 5.48, $C_9H_{25}Si_2Br_2Sb$. Calc.: C, 22.95; H, 5.35%.

3.3. Synthesis of dimethyl[bis(trimethylsilyl)methyl]-antimony(V) diiodide (**3**)

$Me_2[Me_3Si)_2CH]Sb$ (1.5 g, 4.82 mmol) was reacted with I_2 (1.22 g, 4.82) in 15 ml Et_2O in a similar way as described above for the synthesis of **2**. About 2.68 g (98.5%) of yellow crystals of **3** (m.p. 116 – 118 °C) were obtained. ^1H-NMR (C_6D_6, 200 MHz): 0.22 (s, 18 H, CH_3), 2.47 (s, 1H, CH), 2.60 (s, 6 H, CH_3). ^{13}C-NMR (C_6D_6, 50 MHz): 3.00 (CH$_3$–Si), 36.17 (CH), 36.42 (CH$_3$). MS (EI, 70 eV): 437 (98), [M$^+$–Me], 407 (10), [M$^+$–I–2Me], 310 (6) [M$^+$–2I], 129 (31) [(Me$_3$Si)$_2$CH$^+$–2Me], 73 (100) [Me$_3$Si$^+$]. Anal. Found: C, 20.12; H, 4.69, $C_9H_{25}Si_2I_2Sb$. Calc.: C, 19.13; H, 4.46%.

3.4. Synthesis of tris[(trimethylsilyl)methyl]antimony bromide hydroxide (**4**)

3.4.1. By hydrolysis of **1**

35 mg (0.046 mmol) $[(Me_3Si)_2CH]_3SbBr_2$ in 5 ml Et_2O was added to 1 ml of a solution of KOH (1%) in water. After stirring for 2 h the organic phase was

separated and washed twice with 5 ml of diethyl ether. The organic phases were dried with Na_2SO_4. Crystals of **4** (154 mg, 70%) were obtained by slow evaporation of the diethylether solution and used for X-ray diffractommetry.

3.4.2. By hydrolysis of $(Me_3SiCH_2)_3SbBr_2$

6.5 ml of a solution of KOH (1%) in water was added to a solution of $(Me_3SiCH_2)_3SbBr_2$ [14] (0.63 g, 1.16 mmol) in Et_2O (40 ml). After stirring for 4 h the organic phase was separated and the water phase was washed twice with 50 ml of diethyl ether. The organic phases were dried with Na_2SO_4. The solvent was removed in vacuum and the remaining white solid was washed twice with 5 ml of petroleum ether. Crystals of **4** (0.4 g, 72%, m.p. 120–123 °C) were obtained by slow evaporation of the petroleum ether solution. ^{1}H-NMR (C_6D_6, 200 MHz): 0.20 (s, 27 H, CH_3, $^2J_{SiH} = 6.7$ Hz, $^1J_{CH} = 117.5$ Hz), 1.81 (s, 6 H, CH_2). ^{1}H-NMR (CDCl$_3$, 200 MHz): 0.27 (s, 27 H, CH_3, $^2J_{SiH} = 6.5$ Hz, $^1J_{CH} = 119.7$ Hz), 1.78 (s, 6 H, CH_2). ^{13}C-NMR (C_6D_6, 50 MHz): 0.88 (s, 27 H, CH_3), 27.11 (s, 6 H, CH_2). MS (CI$_{neg}$, NH$_3$): 465 (100) [M$^-$–Me], 421 (7) [M$^-$–4Me], 393 (43) [M$^-$–CH$_2$SiMe$_3$], 319 (7) [(Me$_3$SiCH$_2$)$_2$SbBr-(OH)$^-$–Me$_3$Si]. IR (CH$_2$Cl$_2$): 3632 sh v(O–H), 848 vs. δ(Sb–O–H), 542 m v(Sb–O); (Nujol): 3446 br v(O–H), 841 vs δ (Sb–O–H), 581 m v(Sb–O) cm^{-1}. Anal. Found: C, 29.88; H, 7.03. C$_{12}$H$_{34}$Si$_3$BrOSb. Calc.: C, 30.01; H, 7.13%.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC-174048 for compound **1**, CCDC-174051 for compound **3**, CCDC-174049 for compound **4** and CCDC-174050 for compound **5**. Copies of this information can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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